Usage Report for Fiscal Year 2024

Project Title: Development of new long-range corrected density functional theory and its applications

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1. Background and purpose of the project, relationship of the project with other projects

Since advances in core-electron spectroscopies, such as X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS), quantum chemical calculation methods specialized for core-excitation calculations have been explosively developed. However, their high computational costs are an obstacle to be applied to large systems. Delta self-consistent-field (ΔSCF) method based on density functional theory (DFT), which calculates the core-excitation and binding energies by using the total energy difference between the ground and the core hole states, showed reasonable results without relying on exchange–correlation functionals, while convergence difficulties related to a variational collapse often arise from neutral excitation. A dozen years ago, we proposed incorporating the short-range Hartree-Fock (HF) exchange integral using the two-electron Gaussian operator in the long-range corrected (LC) scheme, which can flexibly include the HF exchange and named it LCgau-core-BOP. We demonstrated that LCgau-core-BOP functional which includes the short-range HF exchange improves core-excitation energies of the 2nd-row atoms by reduction of self-interaction error in the 1s orbital.

In this project, we tried to solve the problem that time-dependent LC-DFT cannot simultaneously calculate core excitations from the 3rd-row atoms as well as the 2nd-row atoms by adding the short-range HF exchange using double two-electron Gaussian attenuation functions while it can calculate valence-valence excitations in high accuracy. Since core orbitals of the 3rd-row atoms are more contracted to nuclei for its large nuclear charges, a Gaussian HF attenuation function with a large exponent is expected to improve efficiently core orbital energies of the 3rd-row atoms without changing the core orbitals of the 2nd-row atoms by decreasing short-range self-interaction error residing near nuclei.

2. Specific usage status of the system and calculation method

In this project, we used 11.0% of mpc (245244.9 hours) for this project and other researches which will be submitted to publications.

3. Result

To increase the amount of HF exchange inclusion in the range of 0 ~ 0.2 a.u., we added one of the Gaussian functions with α and ß parameters to include HF exchange at a distance ranging from 0 to 0.2 a.u. for increasing the accuracy of 1s orbital energy of the 3rd-row atoms and the other Gaussian function with α' and β' parameters to include HF exchange at a distance ranging from 0.2 to 0.6 a.u. with the μ parameter (μ = 0.42) fixed for maintaining the accuracy of 1s orbital energy of the 2nd-row atoms of the LC2gau shown in Figure 1, Hence, we obtained the optimized parameters (α = 63.00, β = 10.90, α' = 2.17, and β' = 1.71) of two Gaussian functions that give deviations less than 1.0 eV for the experimental core-excitation energies from 1s orbitals of both the 2nd- and 3rd-row atoms. We call this LC2gau functional with these new parameters "LC2gau-core-BOP". LC2gau-BOP(test) with α = 63.00, β = 6.16, α' = 2.99, and β' = 2.00 parameters was designed to illustrate the effect of including HF exchange in the range of 0 to 0.2 a.u. on core excitation energy calculations from 1s orbitals of the 3rd-row atoms.

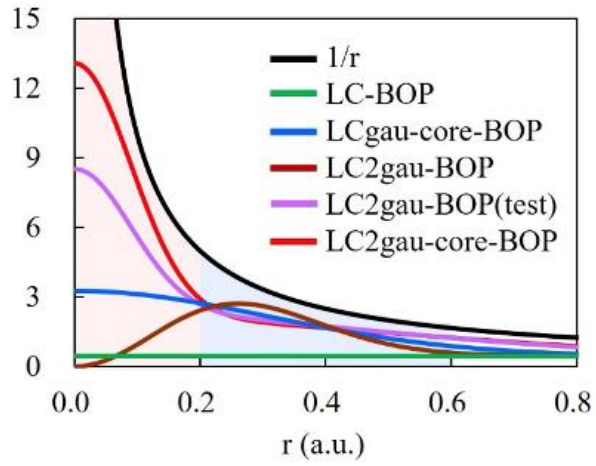

Figure 1. Modified forms of the $1/r_{12}$ operator for the HF exchange contribution in LC-BOP, LCgau-core-BOP, LC2gau-BOP, LC2gau-BOP(test), and LC2gau-core-BOP.

Figure 2 shows that including HF exchange within a specific range improves the accuracies of hybrid DFT functionals for core excitation energies from 1s orbitals of the 2nd- and 3rd-row atoms. LCgau-core-BOP and LC2gau-BOP provide successfully low MAEs below 1.0 eV for the 2nd-row atoms. Finally, LC2gau-core-BOP provides highly accurate core-excitation energies from 1s orbitals of both the 2nd- and 3rd-row atoms.

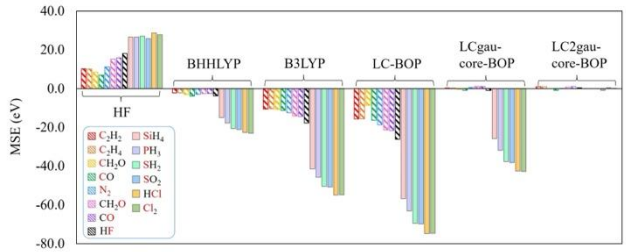

Figure 3. Mean signed errors for the core excitation energies from 1s orbitals of the 2nd-row atoms (in C_2H_2, C_2H_4, CH_2O, CO, N_2, and HF molecules) and the 3rd-row atoms (in SiH_4, PH_3, SH_2, SO_2, HCl, and Cl_2 molecules) according to HF, BHHLYP, B3LYP, LC-BOP, LCgau-core-BOP, and LC2gau-core-BOP.

4. Conclusion

The LCgau-core-BOP, which uses an additional Gaussian attenuating HF exchange integral to long-range correction HF exchange, reproduced core-excitation energies from 1s orbital of the 2nd-row atoms as well as the thermochemical properties with high accuracy but underestimated the core-excitation energies from 1s orbital of the 3rd-row atoms in the SiH_4, PH_3, SH_2, SO_2, HCl, and Cl_2 molecules. In this project, our newly developed LC2gau-core-BOP, which contains one more additional Gaussian attenuating HF exchange to LCgau-core-BOP to include HF exchange especially in the short-range region of 0 ~ 0.2 a.u., provides core-excitation energies from 1s orbitals of the C, N, O, F, Si, P, S, and Cl atoms in the tested molecules in high accuracy. Although numerous methods are being studied to calculate core-excitation energies accurately, our method is a simple and competitive method to accurately calculate core-excitation energies while fundamentally trying to solve self-interaction errors without complex formulas, additional calculations, and specific energy shifts.

5. Schedule and prospect for the future

In the next year, we plan to perform assessment calculations for our newly developed linear-scaling DFT method. In addition, we hope to develop LC3gau-core-BOP functional which can calculate core excitation energy from higher row element in high accuracy.

Fiscal Year 2024 List of Publications Resulting from the Use of the supercomputer

[Paper accepted by a journal]

1. “Long-range Corrected Density Functional Theory Including a Two-Gaussian Hartree–Fock Operator for High Accuracy Core-excitation Energy Calculations of Both the Second- and Third-Row Atoms (LC2gau-core-BOP)” Dae-Hwan Ahn, Takahito Nakajima, Kimihiko Hirao, and Jong-Won Song* J. Chem. Theory Comput. 20, 7113 (2024) [DOI: 10.1021/acs.jctc.4c00651].
2. “Why Does the Optimal Tuning Method of the Range Separation Parameter of a Long-Range Corrected Density Functional Fail in Intramolecular Charge Transfer Excitation Calculations?” Han-Seok Bae, Dae-Hwan Ahn, and Jong-Won Song* Molecules 29, 4423 (2024) [DOI: 10.3390/molecules29184423].

[Conference Proceedings]

[Oral presentation]

[Poster presentation]

[Others (Book, Press release, etc.)]